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(54) **Agent for reducing detergent irritation to skin and eyes**

(57) A water-soluble, positively charged, partially hydrolyzed, protein fraction containing a high concentration of basic amino acids, having a pI of 7—12, a Bloom gel value of zero and a molecular weight of 600 to 12,000 is disclosed together with liquid detergent compositions having reduced skin and eye irritation properties which contain 10% to 50%, by weight, of a water-soluble, skin-irritating anionic detergent and 0.2% to 5%, by weight, of the said protein fraction in an aqueous vehicle.

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SPECIFICATION

Agent for reducing detergent irritation to skin and eyes

The present invention relates to novel light duty liquid detergent compositions useful as dishwashing liquids, shampoos, and the like, which are substantially non-irritating to the skin and eyes, comprising an anionic surfactant and a positively charged, water soluble, partially hydrolyzed, protein fraction containing a high concentration of basic amino acids which is obtained by extraction from a partially hydrolyzed protein mixture. Separation of proteins, based on charge, can be obtained by means of batch phase, ion exchange treatment or column ion exchange chromatography utilizing an anionic exchange resin.

Liquid detergents containing anionic surface active agents, such as dishwashing products, are known to contribute to skin damage such as chapping. Similarly, shampoos containing anionic surface active agents cause skin and eye irritation. Non-ionic surface active agents cause little or no skin and eye irritation, so they may and have been used instead. However, the non-ionics are inferior to anionic agents both in foaming power and detergency.

It has been found that the addition of a partially hydrolyzed protein fraction rich in positively charged amino acids, having an isoionic point of 7 to 11 and a Bloom gel value of zero, to an anionic surface active agent-containing composition results in a reduction of skin and eye damage, but surprisingly not a concomitant loss in foaming power or detergency. This discovery has provided a means of retaining the mildness of the non-ionics, and maintaining the foaming power and detergency of anionic surface active agents.

The prior art recognizes the problem of skin and eye irritation of detergent compositions such as dishwashing liquids and shampoos containing surfactants, especially the anionic surfactants, as disclosed in U.S. Patents No. 4,087,518, No. 4,115,548, No. 4,195,077, No. 4,076,800, and British Patents No. 1,478,014, and No. 1,529,841. All of these patents taught reduction of the problem of the deleterious effects of detergents on the skin by adding modified proteins obtained by the chemical modification of a precursor protein, such as by the esterification or amidation of the carboxylic acid groups of the protein to obtain a highly positively charged modified protein as disclosed by U.S. Patent No. 4,115,548; or by the acylation of the primary amino groups of the protein to obtain a highly negatively charged modified protein as disclosed by British Patent No. 1,529,841.

U.S. Patent No. 3,548,056 taught reduction of the skin irritation effects of detergent compositions by the addition of a water-soluble, partially degraded protein such as peptones which may be a partially enzymatically hydrolyzed protein or a heat derived product of protein, to the surfactant-containing composition.

U.S. Patent No. 4,140,759 taught reduction of the skin irritation properties of shampoos by using a lipo-protein detergent complex which is mild to the hair and scalp.

U.S. Patent No. 3,898,186 discloses a mild liquid dishwashing composition containing a specified surface active system which includes a gel-forming gelatin, obtained by the selective hydrolysis of collagen, having a Bloom strength of 50—300 and an isoelectric point between pH 4.6 and 5.0; two anionic surfactants and an amine oxide.

Other protein-containing cosmetic compositions are disclosed in U.S. Patent No. 3,628,974, wherein the said compositions contain a gel-forming, microcrystalline, water-insoluble partial salt of collagen, formed by treating undenaturated collagen with dilute acid solutions having a pH of 1.6 to 2.6; a wrinkle-decreasing aqueous solution of alpha-lactalbumin per se or in combination with beta-lactalbumin, is disclosed in U.S. Patent No. 3,364,118; and a hair spray containing an abietic acid condensate of a protein hydrolysate, is disclosed in U.S. Patent No. 4,229,429. Crotein Q, a product of Croda Inc. of New York, is a cationic quaternary derivative of hydrolyzed collagen protein, and had been used as an ingredient in hair cream rinses and other compositions containing anionic and other surface active agents.

However, none of the above cited prior art discloses a shampoo or a light duty liquid detergent composition having reduced or low skin irritation effects comprising an anionic surfactant and a minor amount of a water soluble, partially hydrolyzed, protein fraction rich in positively charged amino acids, having an isoionic point greater than 7 and a Bloom gel value of zero. The particular hydrolyzed protein fraction used herein, substantially differs from the prior art chemically-modified proteins, partially degraded proteins, lipoproteins and protein reaction products.

It has been found that a light duty liquid detergent composition, comprising an anionic surfactant and a partially hydrolyzed protein fraction, rich in positively charged amino acids, having an isoionic point of 7 to 11 and a Bloom gel value of zero, counters the irritation to the skin and eyes caused by the anionic surfactant, without decreasing the foaming and detergency properties imparted to the composition by the said anionic surfactant.

The present invention aims to provide a light duty liquid detergent having reduced or low skin irritation effects containing anionic surfactant and a partially hydrolyzed protein fraction rich in positively charged amino acids.

The present invention also aims to provide a dishwashing liquid which is of much reduced irritation or substantially non-irritating to the skin.

The invention also aims to provide a shampoo composition which is of much reduced irritation or substantially non-irritating to the skin and eyes.

This invention also aims to provide a light duty liquid detergent wherein the foaming and detergency properties of the anionic surfactant are not significantly decreased by the presence of the water soluble partially hydrolyzed protein fraction having a high concentration of basic amino acids, and an isoionic point of 7 to 11.

According to the present invention a novel light duty liquid detergent comprises an anionic surface active agent and a positively charged, partially hydrolyzed, protein fraction containing high concentrations of basic amino acids and having an isoionic point above 7, specifically 7 to 11, and a Bloom gel value of zero, in an aqueous vehicle.

More specifically, the present invention relates to a liquid detergent composition comprising a skin irritating anionic surface active agent and about 0.2—5% of a positively charged, partially hydrolyzed, protein fraction containing high concentrations of basic amino acids obtained by extraction from a partially hydrolyzed protein mixture and isolation by ion exchange treatment with an anion exchange resin.

The novel, positively charged, protein hydrolysate fraction of the present invention which contains a high concentration of basic amino acids, has an isoionic point greater than 7, a Bloom gel value of zero and a molecular weight of about 600 to 12,000. It can be obtained as a solid powdered material soluble in an aqueous vehicle. When used in a light duty liquid detergent composition it preferably constitutes about 0.2 to 5%, preferably 0.7 to 1.3%, by weight of the light duty liquid detergent which preferably contains about 10—50% by weight of an anionic surfactant as the active ingredient. The positively charged protein hydrolysate fraction reduces the skin and eye irritation effects of the anionic surfactant without decreasing the foaming and detergency properties of the composition.

The positively charged, partially hydrolyzed, protein fraction having a high concentration of basic amino acids of the present invention may be prepared by extraction from a hydrolyzed protein mixture and isolation of the positively charged fraction by means of ion exchange treatment with an anion exchange resin. More specifically, the said protein mixture may be treated with an anion exchange resin, followed by dialysis. The hydrolysate fraction may be used as such or may optionally be freeze dried to remove the water therefrom.

Thus in a preferred form of the invention a method of preparing the said protein fraction comprises the steps of (a) adjusting the pH of a hydrolyzed collagen protein mixture, containing a high concentration of basic amino acids and having a molecular weight of about 600 to 12,000, to the range of 7 to 12; (b) treating the mixture of step (a) with an anionic ion exchange resin to absorb negatively charged groups from the protein onto the resin and to substitute the negatively charged groups from the said resin therefor; (c) dialyzing the mixture from step (b) to remove the said negatively charged groups; and (d) recovering the said protein fraction having a pI point greater than 7.

The protein mixture may be an animal collagen hydrolysate, resulting from the hydrolysis of a protein with an acid or base or an enzyme. When the protein is hydrolyzed by an acid or base, it is necessary to remove the salts (NaCl) formed during the said hydrolysis, prior to treatment of the said protein hydrolysate mixture with the anion exchange resin. The salts can be removed by dialysis of the protein hydrolysate mixture. The source of the animal collagen hydrolysate may be leather scraps, pigs feet and hooves, bones, skin or feet of pork of beef. Commercial products such as Stepan (Registered Trade Mark) PP 37, from Stepan Chemical Co., Chicago, Illinois, an animal collagen hydrolysate from leather scraps hydrolyzed at high pH ($Ca[OH]_2$); and Lexein (Registered Trade Mark) 100P from Inolex Corporation, Chicago, Illinois, an animal collagen hydrolysate from pigs feet and hooves, hydrolyzed by means of steam and/or acid followed by enzyme treatment, are typically collagen protein mixtures from which the novel, positively charged, protein hydrolysate fractions of the present invention may be extracted and isolated.

More specifically, the process of preparing the positively charged, protein hydrolysate fraction containing a high concentration of basic amino acids of the present invention comprises the steps of treating a partially hydrolyzed protein mixture with an anionic exchange resin to absorb negatively charged groups from the protein onto the resin and to substitute acetate groups or other negatively charged groups from the resin therefor and dialyzing the resultant anion-exchanged, protein hydrolysate solution to remove the said resin-substituted, negatively charged groups. A preferred additional first step comprises dialysis of the hydrolyzed protein mixture prior to treatment with the anion exchange resin in order to remove salts and other impurities which may be present as a result of protein hydrolysis. An optional additional final step comprises freeze drying the positively charged protein hydrolysate fraction to remove the water therefrom and preserve it for future use. Ion exchange chromatography is a well known procedure described in the prior art. The bath phase ion exchange chromatography procedure for separation of proteins, based on charge, is described in an article by S. M. Vratsanos and I. D. Mandel entitled "Isolation of Cationic Salivary Proteins" in the *Journal of Dental Research*, Volume 56, B 109, Special Issue B, 1977. The column ion exchange chromatography method is described in a 1973 brochure by Pharmacia Fine Chemicals entitled "Sephadex (Registered Trade Mark) Ion Exchangers — A Guide to Ion Exchange Chromatography". The optimal ratio of ion exchange resin to protein for fractionation of a hydrolyzed protein mixture by ion exchange

chromatography is approximately 20:1. This represents the ratio of resin to protein required to just absorb the anionic proteins onto the resin, but not absorb the neutral or cationic proteins.

Any suitable anion exchange resin may be utilized in the process of producing the positively charged, protein hydrolysate fractions containing a high concentration of basic amino acids. The polystyrene- and polysaccharide-based anion exchangers are most often used. The most important class of anion-exchange resins is based on the introduction of basic groups such as quaternary amino groups into a styrene-divinylbenzene copolymer after polymerization. These are strongly basic anion exchange resins. Examples of strong base anion exchangers are Dowex 1 and 2 resins of Dow Chemical Company; Amberlite IRA 401 and 410 resins of Rohm and Haas Company; De-Acidite FF and Duolites A-40 and A-42 of Diamond Shamrock Company; and Bio-Rad AG 1 resin of Bio-Rad Company. Weak base anion exchangers have primary or secondary amino groups attached to the polymer lattice. Commercially available weak base anion exchangers include Dowex 3, Amberlite IR-45, De-Acidite G and Duolite A-14. Cellulose anion exchangers such as diethylaminoethyl- (DEAE-) and epichlorhydrintriethanolamine (ECTEOLA-) cellulose, may also be used in the fractionation process.

The positively charged, protein hydrolysate fractions of this invention are rich in positively charged amino acids as determined by their high isoionic points of about 7 to 11, whereas, proteins presently in use commercially, have isoionic points between 4 and 5. The hydrolyzed protein mixtures from which the present novel, positively charged, protein hydrolysate fractions are extracted, such as Lexein 100P and Stepan PP 37, have isoionic points of 4.8 and 4.3 respectively. The isoionic point (pI) is measured on a protein which has been thoroughly freed of all non-colloidal ions except hydrogen or hydroxide ions. It is the pH of the pure protein in distilled water. Proteins generally contain a mixture of basic amine and imine groups and acidic carboxylic groups, in the form of basic and acidic amino acids. Proteins rich in basic groups are more positively charged and exhibit high pI values; whereas, proteins rich in acidic groups will be less positively charged and exhibit low pI values. The positive charges are caused mainly by the arginine, lysine and histidine moieties. The negative charges are caused mainly by the aspartic and glutamic acid moieties. The overall charge is caused mainly by the ratio of the positively charged moieties to the negatively charged ones. Hence, a molecule rich in arginine, lysine and histidine moieties and poor in aspartic and glutamic acid moieties would have a high positive charge. For example, glycylarginine has a positively charged group and no negatively charged group, and, therefore, its positive charge is very high (pI 11). In order to obtain a protein hydrolysate fraction which contains the compound glycylarginine, the protein hydrolysate should not be dialyzed prior to being contacted with the anion exchange resin because the glycylarginine would be removed along with the inorganic salts by passing through the dialysis membrane. However, since approximately 33% of collagen is the glycine moiety, a high pI probably indicates a significant concentration of glycylarginine moieties in the positively charged, ion exchange fraction.

It has unexpectedly been found that a correlation exists between the anti-irritant properties of a glycylarginine and the positively charged protein fractions and their pI value as evidenced by Tables 1 and 2, using both in vitro and in vivo tests. The in vitro test measures the degree of curling of epidermis strips (2.5 cms by 0.5 cms) immersed in test solutions, by measuring the width of the strip at its narrowest point where curling is most pronounced. In this test celluloid tabs are glued to each end of the strip with duco cement. Then the strip is suspended by means of a hook through the tab at one end of the strip in water at 6°C for about sixteen hours, removed from the water and suspended in the test solution for a period of time up to forty-eight hours sufficient to yield a meaningful change in the strip. While immersed, the strip is measured at its narrowest point either directly with a ruler or indirectly by measuring the image on a photograph. The aqueous test solutions in Table 1 containing 0.15% LAS (sodium linear C_{10}—C_{13} alkyl benzene sulphonate) and 0.10% protein are adjusted to pH 5.3 and the strips are soaked therein at room temperature for two days prior to measuring the narrowest part of the epidermis strip. The in vivo test is a skin patch test performed on guinea pigs, using 0.20% LAS and 0.10% protein in an aqueous solution.

TABLE 1

Test Material	Isoionic Point (pI)	AII[1]	In Vitro (cm)[2]
H_2O	—	2.40	0.70
LAS + Inolex Collagen Hydrolysate, fraction B[3]	8.7	1.00	0.81
LAS + Inolex Collagen Hydrolysate, fraction A[3]	8.3	0.60	0.65
LAS + Inolex Collagen Hydrolysate, fraction C[3]	7.7	—	0.74
LAS + unfractionated Inolex Collagen Hydrolysate	4.8	0.20	0.40
LAS + Inolex Collagen Hydrolysate, fraction D[4]	3.7	—	0.24
LAS + Inolex Collagen Hydrolysate, fraction E[4]	3.5	−0.60	0.22
LAS	—	0.00	0.23

NOTES ON TABLE 1

[1] This is the guinea pig patch test anti-irritation index. The higher the score, the more effective the material

$$[\text{All Score}_{\text{LAS}} - \text{Score}_{(\text{LAS+Protein})}].$$

A negative All Score indicates that the additive caused increased irritation over and above that caused by LAS.

[2] These are widths at the narrowest point in centimeters (cm) of test skin strips determined in the in vitro epidermis curling test resulting from degrees of tissue torsion; the higher the value, the more effective the material is in preventing skin curling by detergents.

[3] This is a positively charged protein hydrolysate fraction obtained by an anion exchange of dialyzed Lexein 100P using BioRad AG 1 resin acetate (50—100 mesh (U.S. Sieve sizes — the openings being 0.30 to 0.15 mms across)) at a specific pH followed by neutralization to pH 7 with dilute hydrochloric acid, dialysis and lyophilization. Fraction A represents the filtrate obtained at pH 10. Fraction B represents the filtrate obtained at pH 12. Fraction C represents the filtrate obtained at pH 8.

[4] This is a negatively charged protein hydrolysate fraction obtained by anion exchange of dialyzed Lexein 100P using BioRad AG 1 resin acetate (50—100 mesh (U.S. Sieve sizes — the openings being 0.30 to 0.15 mms across)) at a specific pH followed by neutralization to pH 7 with dilute sodium hydroxide, dialysis and lyophilization. Fraction D represents the material retained by the resin at pH 2. Fraction E represents the material retained by the resin at pH 4. Materials retained by the resin were removed using 2 molar sodium chloride solution.

TABLE 2

Test Material	Isoionic Point (pI)	In Vitro (cm)[2]
H_2O	—	0.70
LAS + Glycylarginine	11 (calc.)	0.84
LAS	—	0.23

NOTES ON TABLE 2

[2] As note 2) on Table 1.

These Tables 1 and 2 clearly show decreasing epidermis curling with increasing cationicity (higher isoionic points).

Further verification of the anti-irritant activity was determined by way of primary dermal and eye irritation studies on rabbits.

Additional evidence of the anti-irritant properties of the positively charged, protein fractions of this invention on triethanolamine lauryl sulphate (TEALS) and on sodium lauryl sulphate (SLS) is set forth in Tables 3 and 4 which follow. The test materials comprise 0.5% by weight of either TEALS or SLS and 0.1% by weight of the protein fraction.

TABLE 3
In Vitro Epidermis Curling Test

Test Material	Isoionic Point (pI)	Comparative Ranking (in vitro)[1)]
TEALS + Glycylarginine (dipeptide)	11.0	1
TEALS + Inolex Collagen Hydrolysate Fraction A	8.3	2
TEALS + Inolex Collagen Hydrolysate Fraction B	8.7	3
TEALS + Inolex Collagen Hydrolysate Fraction C	7.7	4
TEALS + Whole Inolex Collagen Hydrolysate Mixture	4.8	5
TEALS (triethanolammonium lauryl sulphate)	—	6
TEALS + Inolex Collagen Hydrolysate Fraction D	3.7	7
TEALS + Inolex Collagen Hydrolysate Fraction E	3.5	8

NOTE ON TABLE 3

[1)] Test skin strips from in vitro epidermis curling test were ranked based upon the degree of curl as shown by the ratio of the narrowest width to the end width, with the strip having the least curl designated 1 and the strip with the most curl being designated 8. The width of the strip which has curled is measured with a ruler at the point of minimum dimension.

TABLE 4

Test Material	Isoionic Point (pI)	Comparative Ranking (in vitro)[1)]
SLS + Inolex Collagen Hydrolysate Fraction B	8.7	1
SLS + Inolex Collagen Hydrolysate Fraction C	7.7	2
SLS + While Inolex Collagen Hydrolysate Mixture	4.8	3
SLS + Inolex Collagen Hydrolysate Fraction D	3.7	4
SLS (sodium lauryl sulphate)	—	5
SLS + Inolex Collagen Hydrolysate Fraction E	3.5	6

NOTES ON TABLE 4

[1)] Test skin strips from in vitro epidermis curling test were ranked based upon the degree of curl as shown by the ratio of the narrowest width to the end width, with the strip having the least curl designated 1 and strip with the most curl being designated 6.

LAS itself causes severe curling of the epidermis. When an anionic protein fraction is added to the LAS, the protein has no effect. However, when a cationic fraction is added to LAS, the protein dramatically counters the curling effect of the LAS making this strip of epidermis similar to a strip from treatment solely with water. Normally one would expect that positively charged proteins would interact with negatively charged detergent molecules, thereby destroying or reducing any mildness effect cause by the protein. In fact, surprisingly the mixture is mild. Although the cationic proteins neutralize the effect that LAS has on in vitro epidermis, no difference in foam height or number of dishes cleaned has been observed in a conventional dish cleaning test. Furthermore, the cationic proteins actually seem to stabilize the foam height. Table 5 shows the relationship between detergent induced in vivo skin irritation and in vitro epidermis curling. A 10% solution of anionic or nonionic surfactant was used as the test solution for the in vivo test, and a 2.4% solution for the in vitro test.

TABLE 5

Detergent	Skin Irritation[5)]	Curling Ratio[6)]
SLS[1)]	severe within 1 day	0.33
LAS[2)]	severe within 1 day	0.25
Sodium tallow soap	intense by 4th day	0.46
AEOS — 3EO[3)]	mild to moderate by 5th day	0.96
Tween 20[4)]	none after 5 days	0.92

NOTES ON TABLE 5

[1)] Sodium lauryl sulphate.

[2)] Sodium linear C_{12}—C_{14} alkyl benzene sulphonate.

[3)] Ammonium C_{12}—C_{15} alkyl ether triethanoxy sulphate.

[4)] Polyoxyethylene (20) sorbitan monolaurate.

[5)] This is skin irritation observed by a skilled evaluator after application of a solution containing a 10% concentration of the test composition adjusted to neutral pH to the forearm of a subject in a Duhring Chamber for a period of five days, with the solution in the Duhring Chamber being changed daily. Skin irritation observed ranges from severe reaction within one day to no reaction within five days.

[6)] This is the ratio of narrow epidermis width to end width. The lower the number the more curling of the epidermis.

Another essential ingredient of the liquid detergent compositions of the present invention is the anionic surface active agent containing a sulphonate, sulphate, carboxylate or phosphate as the anionic water solubilizing group. Examples of suitable anionic detergents include the soaps, such as the water-soluble salts of higher fatty acids or rosin acids, such as may be derived from fats, oils, and waxes of animal, vegetable or marine origin, e.g. the sodium soaps of tallow, grease, coconut oil, tall oil and mixtures thereof; and the sulphated and sulphonated synthetic detergents, particularly those having about 8 to 26, and preferably about 12 to 22, carbon atoms to the molecule. Examples of suitable synthetic anionic detergents include the higher alkyl mononuclear aromatic sulphonates such as the higher alkyl benzene sulphonates containing from 8 to 16 carbon atoms in the alkyl group in a straight or branched chain, e.g. the sodium salts of decyl, undecyl, dodecyl (lauryl), tridecyl, tetradecyl, pentadecyl, or hexadecyl benzene sulphonate and the C_8—C_{16} alkyl toluene, xylene and phenol sulphonates: C_8—C_{16} alkyl naphthalene sulphonate, ammonium diamyl naphthalene sulphonate, and sodium dinonyl naphthalene sulphonate; sulphated aliphatic alcohols such as sodium lauryl and hexadecyl sulphates, triethanolamine lauryl sulphate, and sodium oleyl sulphate; sulphated alcohol ethers, such as lauryl, tridecyl, or tetradecyl sulphates including 1—5 ethylene oxide moieties; sulphated and sulphonated fatty oils, acids or esters, such as the sodium salts of sulphonated castor oil and sulphated red oil; sulphated hydroxyamides such as sulphated hydroxy-ethyl lauramide; sodium salt of lauryl sulphoacetate; sodium salt of dioctyl sulphosuccinate, and the sodium salt of oleyl methyl tauride.

Also included within the ambit of the invention are the sulphuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids, e.g. coconut oil monoglyceride monosulphate, tallow diglyceride monosulphate; and the hydroxy sulphonated higher fatty acid esters such as the higher fatty acid esters of low molecular weight alkylol sulphonic acids, e.g. oleic acid ester of isethionic acid.

The anionic surfactants most often used are the ammonium, mono-, di-, and triethanolamine, and alkali metal (sodium and potassium) salts of the higher alkyl benzene sulphonates, the higher alkyl sulphates, the higher fatty acid monoglyceride sulphates and the sulphated ethoxylated alcohols and

mixtures thereof.

The light duty liquid detergent compositions of the present invention may also contain conventional additional components such as colouring agents and perfumes; thickeners such as methyl cellulose; hydrotropic materials such as ammonium or sodium toluene or xylene sulphonate; salt; ethyl alcohol; preservatives such as formaldehyde, hydrogen peroxide, methyl, ethyl or propyl p-hydroxy benzoate; foam enhancing agents such as the amine oxides e.g. dimethyldodecyl amine oxide, bis (2-hydroxyethyl) dodecyl amine oxide and N-dodecyl morpholine oxide, and the mono- and di-alkylolamide of C_{10}—C_{14} carboxylic acids such as the diethanolamide of coconut fatty acids, lauric monoethanolamide, myristic mono-3-propaneolamide, capric diethanolamide, lauric myristic mono- and di-ethanolamide. These optional additives preferably do not exceed 5% by weight of the composition.

The light duty liquid detergent compositions of the present invention such as dishwashing liquids or shampoos are readily made by simple mixing methods.

These methods have unexpectedly desirable properties when high pI proteins are added. For example, the high foam quality and cleansing performance of anionic detergents is retained but the skin and eye irritation caused by such anionic detergents is decreased.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

All amounts of various ingredients are by weight unless otherwise specified.

EXAMPLE 1

Lexein 100 P, protein hydrolysate obtained from the Inolex Corporation, was diluted to make a 5% aqueous solution. 75 ml aliquots were placed into each of ten dialysis tubes and placed in an 18 l battery jar containing distilled deionized water at 6°C. The solutions were allowed to undergo equilibrium dialysis for approximately 24 hours. The dialyzed solutions may be lyophilized (freeze dried) and preserved for fractionation in the future, if desired. This dialysis step removes inorganic salts and other impurities, e.g. aminoacids and peptides from the protein hydrolysate.

The dialyzed protein solutions were separated by batch phase ion exchange treatment into fractions according to charge. Six portions of 400 g of water washed Bio-Rad AG 1 resin were adjusted to pH 2, 4, 6, 8, 10 and 12 respectively with dilute HCL or dilute NaOH. Six 1000 ml samples of dialyzed protein solutions produced as described above diluted to 2% were adjusted to pH's corresponding to the six resins. The corresponding pH adjusted resins were added to the corresponding protein solutions, stirred for about one hour and filtered. The pH of each filtrate was adjusted to 7. The resins were each washed with a small amount of water and the washings were added to the corresponding filtrate. The pH of each of the combined filtrates was adjusted to 7. The resin was washed with a 2 M NaCl at pH 7 until protein no longer came off the resin. The ninhydrin test may be used to monitor this (comparison of optical density of 570 nanometers (nm) of test solution with non-exchanged protein). These NaCl washings were also adjusted to pH 7.

The filtrate solutions were equilibrium dialyzed overnight. The NaCl washings were equilibrium dialyzed for one hour periods until there was no meaningful change in the refractive index of the dialysate and then they were dialyzed overnight.

The contents of the dialysis bag which contains the positively charged protein fractions in an aqueous medium and which is an article of commerce in accordance with the present invention may be added directly to the light duty liquid detergent, or may be lyophilized and added as a powder (which is also a product in accordance with the invention) to the detergent composition such as the dishwashing formulations and shampoos in Examples 2—4.

EXAMPLE 2

Dishwashing formulations were made up having ingredients and proportions as set out in Table 6 below.

TABLE 6

Ingredient	Percent
Protein hydrolysate fraction[1]	1.0
LAS[2]	17.0
AEOS[3]	13.0
LMMEA[4]	4.0
Ethyl alcohol	0—5
SXS[5]	0—4
NaCl	0—3
Water	Q.S.

NOTES ON TABLE 6
[1] Inolex Collagen Hydrolysate Fraction A, pI — 8.3.
[2] Sodium linear C_{12}—C_{14} alkyl benzene sulphonate.
[3] Ammonium salt of sulphated ethoxylated (3EO) lauryl alcohol.
[4] Lauric/myristic monoethanolamide.
[5] Sodium xylene sulphonate.

The ingredients were thoroughly mixed in an aqueous vehicle. The resulting products were clear solutions, exhibiting good foaming and detergency properties, and substantially reduced skin irritation, i.e. essentially no erythema of the hands or arms in contact with the dishwashing liquid, in contrast to arms and hands soaked in a composition containing no protein fraction.

EXAMPLE 3

A shampoo formulation was made up having the ingredients and proportions as set out in Table 7 below.

TABLE 7

Ingredient	Percent
Protein fraction[1]	1
Triethanolammonium lauryl sulphate	18
Cocomonoethanolamide	3
Water, perfume, etc.	Q.S.
	100.0

NOTES ON TABLE 7
[1] Inolex Collagen Hydrolysate Fraction A — pI 8.3.
[2] Ethylenediamine tetraacetic acid, tetra sodium salt.

The foregoing shampoo is a clear liquid at room temperature and exhibits reduced irritation in the in vitro epidermis curling test and in the in vivo guinea pig test as compared with a shampoo which does not contain the protein fraction.

The viscosity of the shampoo of Example 3 may be reduced by addition of up to 4% by weight of a solubilizer, e.g. ethanol, or increased by adding up to 4% by weight of a water-soluble thickener, e.g. hydroxypropyl methyl cellulose. Other common ingredients in commercial shampoos such as preservatives, e.g. formaldehyde and chelating agents, e.g. EDTA, may be included in the composition of Example 3 in amounts of up to 1% by weight.

EXAMPLE 4

Shampoo formulations were made up having ingredients and proportions as set out in Table 8 below.

TABLE 8

Ingredient	Percent
Protein fraction[1)]	1
Sodium lauryl sulphate	7.5
Ammonium lauryl triethanoxy ether sulphate	2.5
Lauric/Myristic Diethanolamide	2
Alcohol	0—4
Thickener	0—4
Chelating agent (EDTA sodium salt)	0—1
Preservative (Formalin)	0—1
Fragrance	0—1
Water	Q.S.

NOTE ON TABLE 8

[1)] Inolex collagen hydrolysate fraction C — pI 7.7.

The shampoos of Examples 3 and 4 were prepared by thoroughly mixing the ingredients in the aqueous vehicle, resulting in clear liquid shampoo products of suitable viscosity.

Shampoo products containing the positively charged protein fraction of this invention improve conditioning of the hair and lather well.

Variations in the above formulations may be made. For example, other anionic surfactants such as other higher alkyl benzene sulphonates, fatty acid soaps such as tallow soap, other sulphated alcohol ethers and the like may be substituted for the specific anionic surfactants in the examples.

Likewise, other positively charged protein hydrolysate fractions having a pI above 7 and obtained from other collagen hydrolysate sources may be substituted for the particular fraction used in the examples.

CLAIMS

1. A positively charged, water-soluble, partially hydrolyzed, protein fraction containing a high concentration of basic amino acids, having a pI point of 7 to 12, a Bloom gel value of zero and a molecular weight of about 600 to 12,000.

2. A protein fraction as claimed in Claim 1 in which the said protein fraction has an isoionic point of 7 to 11.

3. A protein fraction as claimed in Claim 2 in which the said protein fraction is obtained by extraction from a partially hydrolyzed protein mixture adjusted to a pH of 7 or more by ion exchange with an anionic exchange resin followed by dialysis.

4. A protein fraction as claimed in Claim 1, 2 or 3 in lyophilized form.

5. A protein fraction as claimed in Claim 1 substantially as specifically described herein.

6. A method of preparing the protein fraction as claimed in any one of Claims 1 to 5 which comprises adjusting the pH of an aqueous hydrolyzed collagen protein composition containing a high concentration of basic amino acids and having a molecular weight of about 600 to 12,000 to the range of 7 to 12; contacting the composition having a pH in the range 7 to 12 with an anionic ion exchange resin to absorb negatively charged groups from the protein onto the resin and to substitute the negatively charged groups from the said resin therefor to produce an ion exchanged protein composition which is dialysed to remove the said negatively charged groups; and recovering the protein fraction having a pI point of 7 to 12.

7. A method as claimed in Claim 8 in which the said anion exchange resin is a strongly basic anion exchange resin.

8. A method as claimed in Claim 6 or Claim 7 in which the resin is maintained in a column and the

composition having a pH in the range 7 to 12 is contacted with the resin by being flowed through the column.

9. A method as claimed in Claim 7 or Claim 8 in which the pH of the composition is adjusted after it has been contacted with the resin prior to it being dialysed.

10. A method as claimed in any one of Claims 6 to 9 which includes, in addition, the step of dialyzing the said hydrolyzed, collagen protein composition to remove salts and other impurities prior to contacting it with the anion exchange resin.

11. A method as claimed in any one of Claims 6 to 10 in which the protein fraction is recovered by freeze drying.

12. A method as claimed in Claim 6 substantially as specifically described herein with reference to Example 1.

13. A protein fraction whenever prepared by a method as claimed in any one of Claims 6 to 12.

14. A liquid detergent composition comprising an aqueous vehicle containing 10% to 50% by weight of a water-soluble, skin-irritating, anionic surfactant and 0.2% to 5%, by weight, of a protein fraction as claimed in any one of Claims 1 to 5 or 13, the said composition exhibiting reduced skin and eye irritation properties due to the presence of the said protein fraction.

15. A liquid detergent composition as claimed in Claim 14 in which the said anionic detergent contains a sulphate or sulphonate group.

16. A liquid detergent composition as claimed in Claim 14 or Claim 15 in which the said protein fraction is present in an amount of 0.7% to 1.3%, by weight.

17. A liquid detergent composition as claimed in Claim 14 substantially as specifically described herein with reference to any one of Examples 2, 3 or 4.

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